

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-042876

(43)Date of publication of application : 08.02.2002

(51)Int.Cl.

H01M 10/40

H01M 4/58

H01M 4/62

(21)Application number : 2000-223789

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(22)Date of filing : 25.07.2000

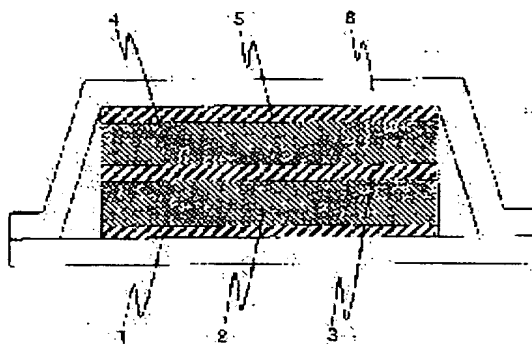
(72)Inventor : KANO GENTARO

## (54) LITHIUM BATTERY

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a lithium battery of high performance with excellent mechanical property and workability in the lithium battery formed by disposing an oxide-based inorganic solid electrolyte having lithium ion conductivity between a positive electrode and a negative electrode.

**SOLUTION:** This lithium battery is formed by disposing the oxide-based inorganic solid electrolyte having lithium ion conductivity between the negative electrode and the positive electrode formed of an active material capable of reversible storage and discharge of lithium ion. A polymer of cyclic ester with C=C unsaturated bond in a ring, or its derivative is interposed between active material grain and oxide-based inorganic solid electrolyte grain.



## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

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CLAIMS

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[Claim(s)]

[Claim 1] The lithium cell characterized by consisting of the polymer of the ester to which the binding material to the particle which constitutes said active material and an oxide system inorganic solid electrolyte is annular, and has a C=C unsaturated bond in endocyclic in the lithium cell which comes to arrange the solid electrolyte which consists of an oxide system inorganic solid electrolyte which has lithium ion conductivity between the positive electrodes and negative electrodes which consist of an active material in which reversible occlusion emission of a lithium ion is possible, or its derivative.

[Claim 2] The lithium cell according to claim 1 with which said oxide system inorganic solid electrolyte is characterized by being a lithium ion conductivity oxide crystal containing a lithium (Li), titanium (Ti), and a Linn (P) and oxygen (O) element.

[Claim 3] The lithium cell according to claim 1 by which it is consisting [ of at least one kind chosen from the group which the active material of said positive electrode and negative electrode becomes from  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  ( $0 \leq x \leq 0.2$ ),  $\text{LiMn}_{2-y}\text{Me}_y\text{O}_4$  (Me=nickel, Zn / Cr, Cu and Zn / ,  $0 \leq y \leq 0.6$ ),  $\text{Li}_4\text{Mn}_5\text{O}_{12}$ , and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  ] characterized.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the lithium cell which comes to arrange the solid electrolyte which consists of an oxide system inorganic solid electrolyte which has lithium ion conductivity between the positive electrodes and negative electrodes which consist of an active material in which reversible occlusion emission of a lithium ion is possible.

[0002]

[Description of the Prior Art] Although there is a lithium cell used as a power source of mobile computing devices, such as a notebook computer and a cellular phone, conventionally, the organic electrolytic solution which dissolved lithium salt in the organic solvent is used for the electrolyte. However, that liquid spill had become a trouble by using this organic electrolytic solution.

[0003] Using a solid electrolyte instead of the organic electrolytic solution is proposed to this trouble.

[0004] There is a solid polymer electrolyte made to dissolve lithium salt, such as  $\text{LiClO}_4$  and  $\text{LiBF}_4$ , in the polyether represented by one of the solid electrolytes at polyethylene oxide or polypropylene oxide.

[0005] In such a giant-molecule solid electrolyte, when a lithium ion moves between a lithium ion and the oxygen atoms which have an interaction, ionic conduction becomes possible.

[0006] However, unless the molecular motion of a polyether is not fully activated at a room temperature, therefore it activates molecular motion at the temperature of 60 degrees C or more, migration of a lithium ion cannot break out easily, and the technical problem that property sufficient as an electrolyte is not acquired occurs.

[0007] Moreover, since a glass transition point becomes high by dissolving lithium salt, the technical problem that molecular motion inactivates also occurs. For example, the ionic conductivity in the room temperature of the solid polymer electrolyte which consists of polyethylene oxide in which  $\text{LiClO}_4$  was dissolved is as low as  $1 \times 10^{-7} \text{ S-cm}^{-1}$ , and it is sharply inferior compared with the ionic conductivity of the organic electrolytic solution being  $1 \times 10^{-3} - 10^{-2} \text{ S-cm}^{-1}$ , and is not yet put in practical use.

[0008] On the other hand, as an example of the lithium cell which used the inorganic solid electrolyte for the electrolyte, the technique using sulfide glass as a solid electrolyte is proposed so that it may be indicated by JP,11-7942,A, for example.

[0009] According to this technique, only a lithium ion contributes to ionic conduction and it has high lithium ion conductivity, but on the other hand sulfide glass is lacking in the stability over moisture or oxygen, and thereby, the manufacture yield falls, consequently it has the technical problem that a manufacturing cost rises.

[0010]  $\text{Li}_{1+(4-n)}\text{xMxTi}_{2-x}(\text{PO}_4)_3$  (M -- a univalent or divalent cation --) proposed by JP,5-299101,A as an example of an oxide system inorganic solid electrolyte n[ when M is univalent and  $n=1$  and M are divalent ] = -- 2 and x can mention  $\text{Li}_{1+x+y}\text{AlxTi}_{2-y}\text{P}_3-y\text{O}_{12}$  ( $0 \leq x \leq 0.4$ ,  $0 < y \leq 0.6$ ) proposed by 0.1-0.5, or JP,10-97811,A.

[0011] A these oxide system inorganic solid electrolyte has the property that the lithium ion

conductivity in a room temperature is equal to  $1 \times 10^{-4} - 10^{-3} \text{ S-cm}^{-1}$ , and the organic electrolytic solution, and moreover, its stability over an environment is high and it is expected as an electrolyte of a lithium cell.

[0012]

[Problem(s) to be Solved by the Invention] However, since said oxide system inorganic solid electrolyte was a brittle material, it was deficient in the mechanical property, and it had the technical problem that the formation of a thin form was difficult.

[0013] It is [ that this technical problem should be canceled ] possible to give flexibility to an oxide system inorganic solid electrolyte.

[0014] That is, when the high molecular compound was mixed, the particle front face of a lithium ion conductivity oxide system inorganic solid electrolyte changed into the condition of having been covered with the insulating high molecular compound, flexibility was given to the oxide system inorganic solid electrolyte, but on the other hand the ionic conduction between the particles of an oxide system inorganic solid electrolyte was checked, and the ionic conductivity of the complex of a lithium ion conductivity oxide inorganic solid electrolyte and a high molecular compound was low.

[0015] This invention is completed in view of the above statement, the purpose is excellent in flexibility, and it is in offering a lithium cell with high charge/discharge capability ability.

[0016]

[Means for Solving the Problem] The lithium cell concerning claim 1 of this invention comes to arrange the solid electrolyte which consists of an oxide system inorganic solid electrolyte which has lithium ion conductivity between the positive electrodes and negative electrodes which consist of an active material in which reversible occlusion emission of a lithium ion is possible, and is characterized by the polymer of the ester which is annular between the above-mentioned active material and an oxide system inorganic solid electrolyte, and has a C=C unsaturated bond endocyclic, or its derivative intervening.

[0017] The lithium cell concerning claim 2 of this invention is characterized by oxide system inorganic solid electrolytes being a lithium (Li), titanium (Ti), and (P) and the lithium ion conductivity oxide crystal containing a Linn oxygen (O) element in the lithium cell of this invention like the above.

[0018] Moreover, the lithium cell concerning claim 3 of this invention is characterized by consisting of at least one kind chosen from the group which the active material of said positive electrode and a negative electrode becomes from  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  ( $0 \leq x \leq 0.2$ ),  $\text{LiMn}_{2-y}\text{Me}_y\text{O}_4$  (Me=nickel, Zn [ Cr, Cu and Zn ],  $0 \leq y \leq 0.6$ ),  $\text{Li}_4\text{Mn}_5\text{O}_{12}$ , and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  in the lithium cell of this invention like the above.

[0019]

[Embodiment of the Invention] Hereafter, the operation gestalt of the lithium cell of this invention is explained. Drawing 1 is the sectional view showing the example of a configuration of the lithium cell concerning this invention.

[0020] As for 1, as for a positive-electrode charge collector and 2, a positive electrode and 3 are [ a solid electrolyte and 4 ] the structures which a negative-electrode charge collector and 6 arranged the solid electrolyte 3 which consists of an oxide system inorganic solid electrolyte which is a battery case and has lithium ion conductivity between a positive electrode 2 and a negative electrode 4, formed the positive-electrode charge collector 1 in the external surface of a positive electrode 2, and formed the negative-electrode charge collector 5 in the external surface of a negative electrode 4 for a negative electrode and 5. And it has surrounded that a battery case 6 is also about this structure.

[0021] The following transition-metals oxides are mentioned as an active material used for a positive electrode 2 and a negative electrode 4.

[0022] For example, a lithium manganese multiple oxide, lithium nickel complex oxide, a lithium cobalt multiple oxide, a lithium nickel cobalt multiple oxide, a lithium vanadium multiple oxide, lithium titanium multiple oxides, etc. and those derivatives are mentioned.

[0023] Among the above-mentioned transition-metals oxides, crystal system with the small volume change of the active material in charge and discharge is the active material of a spinel

system, and especially the group that consists of  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  ( $0 \leq x \leq 0.2$ ),  $\text{LiMn}_{2-y}\text{Me}_y\text{O}_4$  (Me=nickel, Zn [Cr, Cu and Zn],  $0 \leq y \leq 0.6$ ),  $\text{Li}_4\text{Mn}_5\text{O}_{12}$ , and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is good at the point which shows a good cycle property.

[0024] In the oxide system inorganic solid electrolyte used for a solid electrolyte 3 For example, crystalline substance solid electrolytes, such as  $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  and  $\text{Li}_{3.6}\text{germanium}_{0.6}\text{V}_{0.4}\text{O}_4$ , Noncrystalline solid electrolytes, such as  $30\text{LiI}-41\text{Li}_2\text{O}-29\text{P}_2\text{O}_5$ , and  $40\text{Li(s)}_2\text{O}-35\text{B}-2\text{O}_3-25\text{LiNbO}_3$ ,  $10\text{Li}_2\text{O}-25\text{B}-2\text{O}_3-15\text{SiO}_2-50\text{ZnO}$ , Or the mixture or baking object of a crystalline substance solid electrolyte and a noncrystalline solid electrolyte can be mentioned.

[0025] However, it is amorphous, the lithium ion conductivity of the solid electrolyte of an oxide system is about  $-one\ 1 \times 10^{-6}\ \text{S-cm}$  at a room temperature, and the solid electrolyte which fully fulfills a property is not found out. On the other hand, the solid electrolyte of a crystalline substance has the property that the lithium ion conductivity in a room temperature is equal to  $1 \times 10^{-4} - 10^{-3}\ \text{S-cm}^{-1}$ , and the organic electrolytic solution.

[0026] The solid electrolyte of the crystalline substance of lithium ion conductivity which contains a lithium (Li), titanium (Ti), and a Linn (P) and oxygen (O) element especially also in the solid electrolyte of an oxide system with a crystalline substance is desirable at chemical stability and the point that ion conductivity both sides are excellent.

[0027] concrete --  $\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  (M=aluminum and Sc --) Y, La,  $\text{Li}_{1+x}\text{Ti}_{2-x}(\text{PO}_4)_3$ ,  $\text{Li}_{0.5-3x}\text{R}_{0.5+x}\text{TiO}_3$  (R=La) Pr, Nd, Sm,  $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_3-\text{yO}_{12}$ ,  $\text{Li}_{1+(4-n)}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  (M is a univalent or divalent cation), etc. are mentioned.

[0028] As binding material which binds the particle of these positive active material, a negative-electrode active material, and an oxide system inorganic solid electrolyte, it is annular and the polymer of the ester which has a C=C unsaturated bond in endocyclic, or its derivative is used.

[0029] Such a polymer is an ingredient which has the oxygen atom which can be contributed to lithium ion conduction in high density, and has flexibility. In the polymer existing near the point of contact of an active material and an oxide system inorganic solid electrolyte particle, the resistance to the lithium ion conduction between particles is reduced, it is highly efficient and the cell excellent in workability is obtained.

[0030] It is annular, and as ester which is the precursor of said polymer and which has a C=C unsaturated bond in endocyclic, vinylene carbonate, a coumarin, catechol carbonate, phthalide, etc. are mentioned, and alkylation radical vinylene carbonate, alkylation radical catechol carbonate, etc. are mentioned as the derivative, for example.

[0031] As for the above-mentioned annular ester or the endocyclic C=C unsaturated bond of the derivative, it is desirable that it is not resonating structure so that a polymer may be easy to be formed, and it is desirable that it is the carbonate structure of excelling in lithium ion conductivity. Therefore, it is annular and vinylene carbonate or its derivative is desirable especially as the ester which has a C=C unsaturated bond in endocyclic, or its derivative.

[0032] As a polymerization initiator used for the polymerization reaction of the above-mentioned polymer, radical polymerization agents, such as potassium persulfate, sodium persulfate, persulfuric acid hydrogen, azobisisobutyronitril, and benzoyl peroxide, are mentioned, for example.

[0033] Moreover, the plasticizer of a minute amount may be added in order to raise the flexibility of the above-mentioned polymer. As a suitable plasticizer in this case, ethylene carbonate, propylene carbonate, butylene carbonate, gamma-butyrolactone, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 2-dimethoxyethane, 1, 3-dioxolane, a sulfolane, vinylene carbonate, etc. are mentioned. These plasticizers may add an one-sort independent and may carry out concomitant use addition of the two or more sorts if needed.

[0034] As the addition approach of the polymer of a between [ the particles of a positive electrode and a negative-electrode active material, and an oxide system inorganic solid electrolyte ], after pressurization-casting or calcinating the powder of positive active material, an oxide system inorganic solid electrolyte, and a negative-electrode active material to three layers, sinking in, the approach of carrying out a polymerization, etc. are mentioned to this in the precursor of said polymer, for example.

[0035] Moreover, into a positive electrode and a negative electrode, a conductive oxide, a carbon material, and a metal powder may be mixed as an electronic conduction agent. In a conductive oxide,  $\text{SnO}_2$ ,  $\text{In}_2\text{O}_3$ ,  $\text{TiO}_{2-x}$ ,  $\text{ZnO}$  and  $\text{Fe}_3\text{O}_4$ ,  $\text{ReO}_3$ ,  $\text{MoO}_2$ ,  $\text{RuO}_2$ ,  $\text{VO}$ ,  $\text{WO}_2$ , etc. are mentioned, for example.

[0036] As this carbon material, carbon black, the shape of a scale, fibrous natural graphites, artificial graphites, such as furnace black, and acetylene black, thermal black, etc. can be mentioned.

[0037] Furthermore by the metal powder, Au, Ag, aluminum, Cu, nickel, Fe, etc. can be mentioned, for example.

[0038] Moreover, oxide glass may be used in the case of sintering of the particle of positive active material, a negative-electrode active material, and an oxide system inorganic solid electrolyte. As oxide glass, the multicomponent system oxide glass consisting mainly of phosphate glass, borate glass, silicate glass, and borosilicate glass can be mentioned, for example.

[0039] What is necessary is just to constitute that the metallic thin plate used for the positive-electrode charge collector 1 and the negative-electrode charge collector 5 is also for metallic materials, such as stainless steel, aluminum, nickel, copper, covar, 42 alloys, titanium, or an aluminium alloy.

[0040] As a battery case 6, the laminate film which carried out the laminating of aluminium foil and the polyethylene, for example is used.

[0041] In this way, according to the lithium cell of this invention, as binding material which binds the particle of positive active material, a negative-electrode active material, and an oxide system inorganic solid electrolyte, it is annular, and the flexibility which is that the polymer of the ester which has a  $\text{C}=\text{C}$  unsaturated bond, or its derivative used, and was excellent in endocyclic is acquired, and high charge/discharge capability ability can be attained.

[0042]

[Example] Lithium cell A of this invention was produced for vinylene carbonate sinking in and by carrying out a polymerization to the layered product which consists of a positive electrode, a negative electrode, and an oxide system inorganic solid electrolyte.

[0043] The concrete configuration of this lithium cell A is as follows.  $50\text{P}_2\text{O}_5-30\text{PbO}-20\text{ZnO}$  which is  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  and oxide glass which are a positive electrode and a negative-electrode active material was blended dryly by the weight ratio 95:5, and it considered as mixed powder. In addition, TEREPINE oil and toluene were added further, and it mixed so that the ethyl cellulose of a shaping assistant might be set to 10 by the weight ratio to this mixed powder 100, and the slurry was prepared. The positive electrode and the negative-electrode Plastic solid were acquired by carrying out heating baking of what was judged after applying this slurry on the polyethylene terephthalate (PET) film and making it dry at 650 degrees C.

[0044]  $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_3-\text{yO}_{12}$  ( $0 \leq x \leq 0.4$ ,  $0 \leq y \leq 0.6$ ) which is an oxide system inorganic solid electrolyte, and  $50\text{P}_2\text{O}_5-30\text{PbO}-20\text{ZnO}$  which is oxide glass were blended dryly by the weight ratio 90:10, and it considered as mixed powder. In addition, TEREPINE oil and toluene were added further, and it mixed so that the ethyl cellulose of a shaping assistant might be set to 10 by the weight ratio to this mixed powder 100, and the slurry was prepared. After applying this slurry on a positive electrode and a negative-electrode Plastic solid and sticking it, the three-layer layered product was obtained by carrying out heating baking at 600 degrees C.

[0045] The positive electrode and the negative electrode were [ 75 micrometers and the oxide system inorganic solid electrolyte of the thickness of a layered product ] 50 micrometers.

[0046] the benzoyl peroxide which is a radical polymerization initiator at the inside of argon atmosphere, and vinylene carbonate -- 0.5wt(s)% -- after adding, this was infiltrated into the above-mentioned three-layer layered product which performed dehydration processing with vacuum heating. Furthermore, it heated at 60 degrees C among argon atmosphere for 20 hours, polymerization of vinylene carbonate was performed, and the generation-of-electrical-energy component was formed.

[0047] After judging the above-mentioned generation-of-electrical-energy component to 15x20mm, the charge collector of a nickel plate was stuck on the positive electrode and the

negative electrode, and the battery case was formed by carrying out heating weld of the aluminum-polyethylene laminate film. The dimension of a battery case was set to 25x30mm.  
 [0048] As an example 1 of the [example 1 of comparison] comparison, lithium cell B which does not contain the polymer of vinylene carbonate like an example was produced using the same three-layer layered product as the above-mentioned lithium cell A.

[0049] Lithium cell C which contains polystyrene like an example was produced except having sunk in and having carried out the polymerization of the styrene to the interior of a three-layer layered product as an example 2 of the [example 2 of comparison] comparison, using the same three-layer layered product as the above-mentioned lithium cell A.

[0050] About these lithium cells A, B, and C, in order to investigate the flexibility, the bending test was performed. The bending test set the deflection of the direction of a long side to 5mm, performed it 3 times, and viewed the condition of the three-layer layered product inside each cell.

[0051] Consequently, in lithium cell [ of the example of a comparison ] B, the layered product of the lithium cells A and C in this example became clear [ the exterior's abnormalities not being seen but having high flexibility ] also by the bending test to the crack having been looked at by the layered product.

[0052] Moreover, charge-and-discharge measurement was performed about these lithium cells A, B, and C, and discharge capacity was calculated.

[0053] It set the current value to 100microA, having set the charge termination electrical potential difference as 2.0V, and after it carried out constant-current charge, the discharge capacity of each lithium cell was left for 1 hour, and with the current value A of 100micro, to 0V, constant-current discharge of it was carried out, and it calculated it. The result is shown in Table 1.

[0054]

[Table 1]

電池名称	放電容量 (mA h)
リチウム電池A	4. 2
リチウム電池B	動作しない
リチウム電池C	動作しない

[0055] As shown in Table 1, compared with lithium cell C containing lithium cell B and polystyrene which do not contain the polymer of vinylene carbonate for vinylene carbonate by sinking in and lithium cell A which carried out the polymerization, the charge-and-discharge property improved greatly in the three-layer layered product which consists of a positive electrode, a negative electrode, and an oxide system inorganic solid electrolyte.

[0056] this invention person is that the polymer of the vinylene carbonate which has the oxygen atom which can be contributed to lithium ion conduction in high density exists near the point of contact of the particle of an active material and an oxide system inorganic solid electrolyte, and thinks that it is because the resistance to the lithium ion conduction between particles was reduced.

[0057] In addition, this invention is not limited to the above examples of an operation gestalt, and adding modification and amelioration various in the range which does not deviate from the summary of this invention does not interfere at all.

[0058]

[Effect of the Invention] As mentioned above, according to this invention, it sets to the lithium cell which comes to arrange the oxide system inorganic solid electrolyte which has lithium ion conductivity between the positive electrodes and negative electrodes which consist of an active material in which reversible occlusion emission of a lithium ion is possible. Between said active material particle and an oxide system inorganic solid electrolyte particle, it is annular, and when the polymer of the ester which has a C=C unsaturated bond endocyclic, or its derivative intervenes, are highly efficient. And the lithium cell excellent in mechanical characteristics and workability was obtained, and this has attained high charge/discharge capability ability.

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TECHNICAL FIELD

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[Field of the Invention] This invention relates to the lithium cell which comes to arrange the solid electrolyte which consists of an oxide system inorganic solid electrolyte which has lithium ion conductivity between the positive electrodes and negative electrodes which consist of an active material in which reversible occlusion emission of a lithium ion is possible.

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PRIOR ART

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[Description of the Prior Art] Although there is a lithium cell used as a power source of mobile computing devices, such as a notebook computer and a cellular phone, conventionally, the organic electrolytic solution which dissolved lithium salt in the organic solvent is used for the electrolyte. However, that liquid spill had become a trouble by using this organic electrolytic solution.

[0003] Using a solid electrolyte instead of the organic electrolytic solution is proposed to this trouble.

[0004] There is a solid polymer electrolyte made to dissolve lithium salt, such as  $\text{LiClO}_4$  and  $\text{LiBF}_4$ , in the polyether represented by one of the solid electrolytes at polyethylene oxide or polypropylene oxide.

[0005] In such a giant-molecule solid electrolyte, when a lithium ion moves between a lithium ion and the oxygen atoms which have an interaction, ionic conduction becomes possible.

[0006] However, unless the molecular motion of a polyether is not fully activated at a room temperature, therefore it activates molecular motion at the temperature of 60 degrees C or more, migration of a lithium ion cannot break out easily, and the technical problem that property sufficient as an electrolyte is not acquired occurs.

[0007] Moreover, since a glass transition point becomes high by dissolving lithium salt, the technical problem that molecular motion inactivates also occurs. For example, the ionic conductivity in the room temperature of the solid polymer electrolyte which consists of polyethylene oxide in which  $\text{LiClO}_4$  was dissolved is as low as  $1 \times 10^{-7} \text{ S-cm}^{-1}$ , and it is sharply inferior compared with the ionic conductivity of the organic electrolytic solution being  $1 \times 10^{-3} - 10^{-2} \text{ S-cm}^{-1}$ , and is not yet put in practical use.

[0008] On the other hand, as an example of the lithium cell which used the inorganic solid electrolyte for the electrolyte, the technique using sulfide glass as a solid electrolyte is proposed so that it may be indicated by JP,11-7942,A, for example.

[0009] According to this technique, only a lithium ion contributes to ionic conduction and it has high lithium ion conductivity, but on the other hand sulfide glass is lacking in the stability over moisture or oxygen, and thereby, the manufacture yield falls, consequently it has the technical problem that a manufacturing cost rises.

[0010]  $\text{Li}_{1+(4-n)}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  (M -- a univalent or divalent cation --) proposed by JP,5-299101,A as an example of an oxide system inorganic solid electrolyte n[ when M is univalent and  $n=1$  and M are divalent ] = -- 2 and x can mention  $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-y}\text{P}_3-y\text{O}_{12}$  ( $0 \leq x \leq 0.4$ ,  $0 < y \leq 0.6$ ) proposed by 0.1-0.5, or JP,10-97811,A.

[0011] A these oxide system inorganic solid electrolyte has the property that the lithium ion conductivity in a room temperature is equal to  $1 \times 10^{-4} - 10^{-3} \text{ S-cm}^{-1}$ , and the organic electrolytic solution, and moreover, its stability over an environment is high and it is expected as an electrolyte of a lithium cell.

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EFFECT OF THE INVENTION

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[Effect of the Invention] As mentioned above, according to this invention, it sets to the lithium cell which comes to arrange the oxide system inorganic solid electrolyte which has lithium ion conductivity between the positive electrodes and negative electrodes which consist of an active material in which reversible occlusion emission of a lithium ion is possible. Between said active material particle and an oxide system inorganic solid electrolyte particle, it is annular, and when the polymer of the ester which has a C=C unsaturated bond endocyclic, or its derivative intervenes, are highly efficient. And the lithium cell excellent in mechanical characteristics and workability was obtained, and this has attained high charge/discharge capability ability.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, since said oxide system inorganic solid electrolyte was a brittle material, it was deficient in the mechanical property, and it had the technical problem that the formation of a thin form was difficult.

[0013] It is [ that this technical problem should be canceled ] possible to give flexibility to an oxide system inorganic solid electrolyte.

[0014] That is, when the high molecular compound was mixed, the particle front face of a lithium ion conductivity oxide system inorganic solid electrolyte changed into the condition of having been covered with the insulating high molecular compound, flexibility was given to the oxide system inorganic solid electrolyte, but on the other hand the ionic conduction between the particles of an oxide system inorganic solid electrolyte was checked, and the ionic conductivity of the complex of a lithium ion conductivity oxide inorganic solid electrolyte and a high molecular compound was low.

[0015] This invention is completed in view of the above statement, the purpose is excellent in flexibility, and it is in offering a lithium cell with high charge/discharge capability ability.

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MEANS

[Means for Solving the Problem] The lithium cell concerning claim 1 of this invention comes to arrange the solid electrolyte which consists of an oxide system inorganic solid electrolyte which has lithium ion conductivity between the positive electrodes and negative electrodes which consist of an active material in which reversible occlusion emission of a lithium ion is possible, and is characterized by the polymer of the ester which is annular between the above-mentioned active material and an oxide system inorganic solid electrolyte, and has a C=C unsaturated bond endocyclic, or its derivative intervening.

[0017] The lithium cell concerning claim 2 of this invention is characterized by oxide system inorganic solid electrolytes being a lithium (Li), titanium (Ti), and (P) and the lithium ion conductivity oxide crystal containing a Lunn oxygen (O) element in the lithium cell of this invention like the above.

[0018] Moreover, the lithium cell concerning claim 3 of this invention is characterized by consisting of at least one kind chosen from the group which the active material of said positive electrode and a negative electrode becomes from  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  ( $0 \leq x \leq 0.2$ ),  $\text{LiMn}_{2-y}\text{Me}_y\text{O}_4$  (Me=nickel, Zn [ Cr, Cu and Zn ],  $0 \leq y \leq 0.6$ ),  $\text{Li}_4\text{Mn}_5\text{O}_{12}$ , and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  in the lithium cell of this invention like the above.

[0019]

[Embodiment of the Invention] Hereafter, the operation gestalt of the lithium cell of this invention is explained. Drawing 1 is the sectional view showing the example of a configuration of the lithium cell concerning this invention.

[0020] As for 1, as for a positive-electrode charge collector and 2, a positive electrode and 3 are [ a solid electrolyte and 4 ] the structures which a negative-electrode charge collector and 6 arranged the solid electrolyte 3 which consists of an oxide system inorganic solid electrolyte which is a battery case and has lithium ion conductivity between a positive electrode 2 and a negative electrode 4, formed the positive-electrode charge collector 1 in the external surface of a positive electrode 2, and formed the negative-electrode charge collector 5 in the external surface of a negative electrode 4 for a negative electrode and 5. And it has surrounded that a battery case 6 is also about this structure.

[0021] The following transition-metals oxides are mentioned as an active material used for a positive electrode 2 and a negative electrode 4.

[0022] For example, a lithium manganese multiple oxide, lithium nickel complex oxide, a lithium cobalt multiple oxide, a lithium nickel cobalt multiple oxide, a lithium vanadium multiple oxide, lithium titanium multiple oxides, etc. and those derivatives are mentioned.

[0023] Among the above-mentioned transition-metals oxides, crystal system with the small volume change of the active material in charge and discharge is the active material of a spinel system, and especially the group that consists of  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  ( $0 \leq x \leq 0.2$ ),  $\text{LiMn}_{2-y}\text{Me}_y\text{O}_4$  (Me=nickel, Zn [ Cr, Cu and Zn ],  $0 \leq y \leq 0.6$ ),  $\text{Li}_4\text{Mn}_5\text{O}_{12}$ , and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is good at the point which shows a good cycle property.

[0024] In the oxide system inorganic solid electrolyte used for a solid electrolyte 3 For example, crystalline substance solid electrolytes, such as  $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  and  $\text{Li}_{3.6}\text{germanium}_{0.6}\text{V}_{0.4}\text{O}_4$ , Noncrystalline solid electrolytes, such as  $30\text{LiI}-41\text{Li}_2\text{O}-29\text{P}_2\text{O}_5$ , and

40Li(s)2O-35 B-2O3-25LiNbO3, 10Li2O-25 B-2O3-15SiO2-50ZnO, Or the mixture or baking object of a crystalline substance solid electrolyte and a noncrystalline solid electrolyte can be mentioned.

[0025] However, it is amorphous, the lithium ion conductivity of the solid electrolyte of an oxide system is about  $-one\ 1 \times 10^{-6}\ S\text{-cm}$  at a room temperature, and the solid electrolyte which fully fulfills a property is not found out. On the other hand, the solid electrolyte of a crystalline substance has the property that the lithium ion conductivity in a room temperature is equal to  $1 \times 10^{-4} - 10^{-3}\ S\text{-cm}^{-1}$ , and the organic electrolytic solution.

[0026] The solid electrolyte of the crystalline substance of lithium ion conductivity which contains a lithium (Li), titanium (Ti), and a Linn (P) and oxygen (O) element especially also in the solid electrolyte of an oxide system with a crystalline substance is desirable at chemical stability and the point that ion conductivity both sides are excellent.

[0027] concrete --  $Li_{1+x}M_xTi_{2-x}(PO_4)_3$  (M=aluminum and Sc --) Y, La,  $Li_{1+x}Ti_{2-x}(PO_4)_3$ ,  $Li_{0.5-3x}R_{0.5+x}TiO_3$  (R=La) Pr, Nd, Sm,  $Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$ ,  $Li_{1+(4-n)}M_xTi_{2-x}(PO_4)_3$  (M is a univalent or divalent cation), etc. are mentioned.

[0028] As binding material which binds the particle of these positive active material, a negative-electrode active material, and an oxide system inorganic solid electrolyte, it is annular and the polymer of the ester which has a C=C unsaturated bond in endocyclic, or its derivative is used.

[0029] Such a polymer is an ingredient which has the oxygen atom which can be contributed to lithium ion conduction in high density, and has flexibility. In the polymer existing near the point of contact of an active material and an oxide system inorganic solid electrolyte particle, the resistance to the lithium ion conduction between particles is reduced, it is highly efficient and the cell excellent in workability is obtained.

[0030] It is annular, and as ester which is the precursor of said polymer and which has a C=C unsaturated bond in endocyclic, vinylene carbonate, a coumarin, catechol carbonate, phthalide, etc. are mentioned, and alkylation radical vinylene carbonate, alkylation radical catechol carbonate, etc. are mentioned as the derivative, for example.

[0031] As for the above-mentioned annular ester or the endocyclic C=C unsaturated bond of the derivative, it is desirable that it is not resonating structure so that a polymer may be easy to be formed, and it is desirable that it is the carbonate structure of excelling in lithium ion conductivity. Therefore, it is annular and vinylene carbonate or its derivative is desirable especially as the ester which has a C=C unsaturated bond in endocyclic, or its derivative.

[0032] As a polymerization initiator used for the polymerization reaction of the above-mentioned polymer, radical polymerization agents, such as potassium persulfate, sodium persulfate, persulfuric acid hydrogen, azobisisobutyronitril, and benzoyl peroxide, are mentioned, for example.

[0033] Moreover, the plasticizer of a minute amount may be added in order to raise the flexibility of the above-mentioned polymer. As a suitable plasticizer in this case, ethylene carbonate, propylene carbonate, butylene carbonate, gamma-butyrolactone, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 2-dimethoxyethane, 1, 3-dioxolane, a sulfolane, vinylene carbonate, etc. are mentioned. These plasticizers may add an one-sort independent and may carry out concomitant use addition of the two or more sorts if needed.

[0034] As the addition approach of the polymer of a between [ the particles of a positive electrode and a negative-electrode active material, and an oxide system inorganic solid electrolyte ], after pressurization-casting or calcinating the powder of positive active material, an oxide system inorganic solid electrolyte, and a negative-electrode active material to three layers, sinking in, the approach of carrying out a polymerization, etc. are mentioned to this in the precursor of said polymer, for example.

[0035] Moreover, into a positive electrode and a negative electrode, a conductive oxide, a carbon material, and a metal powder may be mixed as an electronic conduction agent. In a conductive oxide, SnO2, In 2O3, TiO2-x, ZnO and Fe 3O4, ReO3, MoO2, RuO2, VO, WO2, etc. are mentioned, for example.

[0036] As this carbon material, carbon black, the shape of a scale, fibrous natural graphites, artificial graphites, such as furnace black, and acetylene black, thermal black, etc. can be

mentioned.

[0037] Furthermore by the metal powder, Au, Ag, aluminum, Cu, nickel, Fe, etc. can be mentioned, for example.

[0038] Moreover, oxide glass may be used in the case of sintering of the particle of positive active material, a negative-electrode active material, and an oxide system inorganic solid electrolyte. As oxide glass, the multicomponent system oxide glass consisting mainly of phosphate glass, borate glass, silicate glass, and borosilicate glass can be mentioned, for example.

[0039] What is necessary is just to constitute that the metallic thin plate used for the positive-electrode charge collector 1 and the negative-electrode charge collector 5 is also for metallic materials, such as stainless steel, aluminum, nickel, copper, covar, 42 alloys, titanium, or an aluminium alloy.

[0040] As a battery case 6, the laminate film which carried out the laminating of aluminium foil and the polyethylene, for example is used.

[0041] In this way, according to the lithium cell of this invention, as binding material which binds the particle of positive active material, a negative-electrode active material, and an oxide system inorganic solid electrolyte, it is annular, and the flexibility which is that the polymer of the ester which has a C=C unsaturated bond, or its derivative used, and was excellent in endocyclic is acquired, and high charge/discharge capability ability can be attained.

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[Translation done.]

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EXAMPLE

[Example] Lithium cell A of this invention was produced for vinylene carbonate sinking in and by carrying out a polymerization to the layered product which consists of a positive electrode, a negative electrode, and an oxide system inorganic solid electrolyte.

[0043] The concrete configuration of this lithium cell A is as follows. 50P2O5-30PbO-20ZnO which is Li<sub>1.1</sub>Mn<sub>1.9</sub>O<sub>4</sub> and oxide glass which are a positive electrode and a negative-electrode active material was blended dryly by the weight ratio 95:5, and it considered as mixed powder. In addition, TEREPINE oar and toluene were added further, and it mixed so that the ethyl cellulose of a shaping assistant might be set to 10 by the weight ratio to this mixed powder 100, and the slurry was prepared. The positive electrode and the negative-electrode Plastic solid were acquired by carrying out heating baking of what was judged after applying this slurry on the polyethylene terephthalate (PET) film and making it dry at 650 degrees C.

[0044] Li<sub>1+x+y</sub>Al<sub>x</sub>Ti<sub>2-x</sub>Si<sub>y</sub>P<sub>3-y</sub>O<sub>12</sub> (0<=x<=0.4, 0<=y<=0.6) which is an oxide system inorganic solid electrolyte, and 50P2O5-30PbO-20ZnO which is oxide glass were blended dryly by the weight ratio 90:10, and it considered as mixed powder. In addition, TEREPINE oar and toluene were added further, and it mixed so that the ethyl cellulose of a shaping assistant might be set to 10 by the weight ratio to this mixed powder 100, and the slurry was prepared. After applying this slurry on a positive electrode and a negative-electrode Plastic solid and sticking it, the three-layer layered product was obtained by carrying out heating baking at 600 degrees C.

[0045] The positive electrode and the negative electrode were [ 75 micrometers and the oxide system inorganic solid electrolyte of the thickness of a layered product ] 50 micrometers.

[0046] the benzoyl peroxide which is a radical polymerization initiator at the inside of argon atmosphere, and vinylene carbonate -- 0.5wt(s)% -- after adding, this was infiltrated into the above-mentioned three-layer layered product which performed dehydration processing with vacuum heating. Furthermore, it heated at 60 degrees C among argon atmosphere for 20 hours, polymerization of vinylene carbonate was performed, and the generation-of-electrical-energy component was formed.

[0047] After judging the above-mentioned generation-of-electrical-energy component to 15x20mm, the charge collector of a nickel plate was stuck on the positive electrode and the negative electrode, and the battery case was formed by carrying out heating weld of the aluminum-polyethylene laminate film. The dimension of a battery case was set to 25x30mm.

[0048] As an example 1 of the [example 1 of comparison] comparison, lithium cell B which does not contain the polymer of vinylene carbonate like an example was produced using the same three-layer layered product as the above-mentioned lithium cell A.

[0049] Lithium cell C which contains polystyrene like an example was produced except having sunk in and having carried out the polymerization of the styrene to the interior of a three-layer layered product as an example 2 of the [example 2 of comparison] comparison, using the same three-layer layered product as the above-mentioned lithium cell A.

[0050] About these lithium cells A, B, and C, in order to investigate the flexibility, the bending test was performed. The bending test set the deflection of the direction of a long side to 5mm, performed it 3 times, and viewed the condition of the three-layer layered product inside each cell.

[0051] Consequently, in lithium cell [ of the example of a comparison ] B, the layered product of the lithium cells A and C in this example became clear [ the exterior's abnormalities not being seen but having high flexibility ] also by the bending test to the crack having been looked at by the layered product.

[0052] Moreover, charge-and-discharge measurement was performed about these lithium cells A, B, and C, and discharge capacity was calculated.

[0053] It set the current value to 100microA, having set the charge termination electrical potential difference as 2.0V, and after it carried out constant-current charge, the discharge capacity of each lithium cell was left for 1 hour, and with the current value A of 100micro, to 0V, constant-current discharge of it was carried out, and it calculated it. The result is shown in Table 1.

[0054]

[Table 1]

電池名称	放電容量 (mA h)
リチウム電池A	4. 2
リチウム電池B	動作しない
リチウム電池C	動作しない

[0055] As shown in Table 1, compared with lithium cell C containing lithium cell B and polystyrene which do not contain the polymer of vinylene carbonate for vinylene carbonate by sinking in and lithium cell A which carried out the polymerization, the charge-and-discharge property improved greatly in the three-layer layered product which consists of a positive electrode, a negative electrode, and an oxide system inorganic solid electrolyte.

[0056] this invention person is that the polymer of the vinylene carbonate which has the oxygen atom which can be contributed to lithium ion conduction in high density exists near the point of contact of the particle of an active material and an oxide system inorganic solid electrolyte, and thinks that it is because the resistance to the lithium ion conduction between particles was reduced.

[0057] In addition, this invention is not limited to the above examples of an operation gestalt, and adding modification and amelioration various in the range which does not deviate from the summary of this invention does not interfere at all.

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[Translation done.]



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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the sectional view showing the example of a configuration of the lithium cell of this invention.

[Description of Notations]

1: A positive-electrode charge collector, 2:positive electrode, 3:solid electrolyte, 4:negative electrode, 5:negative-electrode charge collector, 6 : battery case

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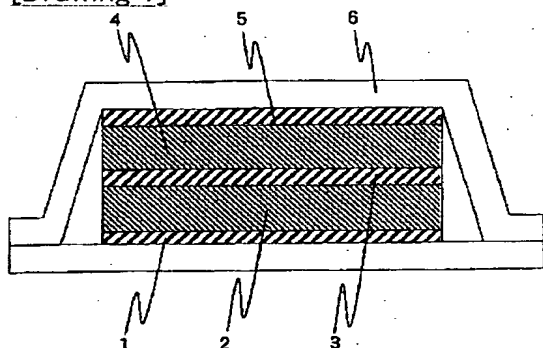
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DRAWINGS

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[Drawing 1]



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[Translation done.]

(19)日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11)特許出願公開番号

特開2002-42876

(P2002-42876A)

(43)公開日 平成14年2月8日(2002.2.8)

(51)Int.Cl. <sup>7</sup>	識別記号	F I	テマコード*(参考)
H 0 1 M 10/40		H 0 1 M 10/40	B 5 H 0 2 9
4/58		4/58	5 H 0 5 0
4/62		4/62	Z

審査請求 未請求 請求項の数3 O L (全 5 頁)

(21)出願番号 特願2000-223789(P2000-223789)

(22)出願日 平成12年7月25日(2000.7.25)

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Fターム(参考) 5H029 AJ01 AJ11 AJ14 AK03 AL03

AM11

5H050 AA01 AA14 AA19 BA17 CA07

CA08 CA09 CB03 DA11 DA13

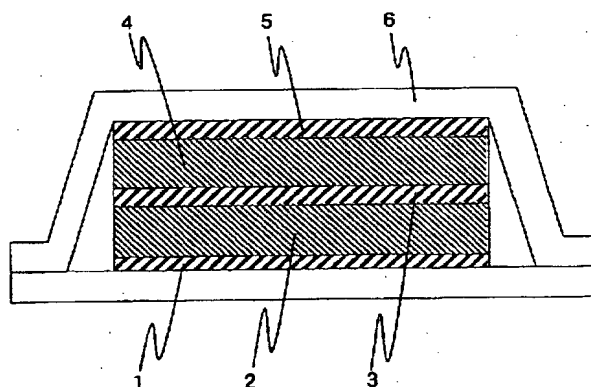
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(54)【発明の名称】 リチウム電池

(57)【要約】

【課題】正極と負極との間にリチウムイオン伝導性を有する酸化物系無機固体電解質を配設してなるリチウム電池において、高性能で、かつ機械的性質、加工性に優れたリチウム電池を提供する。

【解決手段】リチウムイオンの可逆的な吸蔵放出が可能な活物質からなる正極と負極との間にリチウムイオン伝導性を有する酸化物系無機固体電解質を配設してなるリチウム電池において、前記活物質粒子および酸化物系無機固体電解質粒子の間に、環状で環内にC=C不飽和結合を有するエステルまたはその誘導体の重合体を介在させた。



## 【特許請求の範囲】

【請求項 1】リチウムイオンの可逆的な吸蔵放出が可能な活物質からなる正極と負極との間に、リチウムイオン伝導性を有する酸化物系無機固体電解質からなる固体電解質を配設してなるリチウム電池において、前記活物質と酸化物系無機固体電解質を構成する粒子に対する結着材が、環状で環内に C=C 不飽和結合を有するエステルもしくはその誘導体の重合体から成ることを特徴とするリチウム電池。

【請求項 2】前記酸化物系無機固体電解質が、リチウム (Li)、チタン (Ti)、リン (P) および酸素 (O) 元素を含むリチウムイオン伝導性酸化物結晶であることを特徴とする請求項 1 記載のリチウム電池。

【請求項 3】前記正極と負極の活物質が  $Li_{1-x}Mn_{2-x}O_4$  ( $0 \leq x \leq 0.2$ )、 $LiMn_{2-y}Me_yO_4$  ( $Me = Ni, Cr, Cu, Zn, 0 \leq y \leq 0.6$ )、 $Li_xMn_{1-x}O_{12}$  および  $Li_xTi_yO_{12}$  よりなる群から選択される少なくとも 1 種類からなることを特徴とする請求項 1 記載のリチウム電池。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明はリチウムイオンの可逆的な吸蔵放出が可能な活物質からなる正極と負極との間に、リチウムイオン伝導性を有する酸化物系無機固体電解質からなる固体電解質を配設してなるリチウム電池に関するものである。

## 【0002】

【従来の技術】従来、ノートパソコンや携帯電話等のモバイル機器の電源として用いられるリチウム電池があるが、その電解質には、リチウム塩を有機溶媒に溶解した有機電解液が用いられている。ところが、この有機電解液を使用することで、その漏液が問題点となっていた。

【0003】この問題点に対し、有機電解液の代わりに固体電解質を用いることが提案されている。

【0004】固体電解質の一つにポリエチレンオキシドやポリプロピレンオキシドに代表されるポリエーテルに  $LiClO_4$  や  $LiBF_4$  などのリチウム塩を溶解させた高分子固体電解質がある。

【0005】このような高分子固体電解質においては、リチウムイオンと相互作用を有する酸素原子の間をリチウムイオンが移動することによってイオン伝導が可能となる。

【0006】しかしながら、ポリエーテルの分子運動が室温にて十分に活性化されておらず、そのために 60℃ 以上の温度で分子運動を活性化しないとリチウムイオンの移動が起きにくく、電解質として十分な特性が得られないという課題がある。

【0007】また、リチウム塩を溶解することによってガラス転移点が高くなるため、分子運動が不活性化するという課題もある。例えば、 $LiClO_4$  を溶解させた

ポリエチレンオキシドからなる高分子固体電解質の室温でのイオン伝導度は  $1 \times 10^{-7} S \cdot cm^{-1}$  と低く、有機電解液のイオン伝導度が  $1 \times 10^{-3} \sim 10^{-2} S \cdot cm^{-1}$  であることに比べて、大幅に劣り、いまだ実用化されていない。

【0008】一方、電解質に無機固体電解質を用いたリチウム電池の例としては、例えば特開平 11-7942 号公報に開示されるように固体電解質として硫化物ガラスを用いる技術が提案されている。

【0009】この技術によれば、リチウムイオンのみがイオン伝導に寄与し、高いリチウムイオン伝導度を有するが、その反面、硫化物ガラスは水分や酸素に対する安定性に乏しく、これにより、製造歩留まりが低下し、その結果、製造コストが上昇するという課題がある。

【0010】酸化物系無機固体電解質の例としては、特開平 5-299101 号公報で提案された  $Li_{1-(4-m)}M_nTi_{2-m}(PO_4)_3$  ( $M$  は 1 価または 2 価の陽イオン、 $M$  が 1 価のとき  $n=1$ 、 $M$  が 2 価のとき  $n=2$ 、 $x$  は 0.1~0.5) や特開平 10-97811 号公報で提案された  $Li_{1-x-y}Al_xTi_{2-y}P_{3-y}O_{12}$  ( $0 \leq x \leq 0.4$ 、 $0 < y \leq 0.6$ ) を挙げることができる。

【0011】これら酸化物系無機固体電解質は、室温でのリチウムイオン伝導度が  $1 \times 10^{-4} \sim 10^{-3} S \cdot cm^{-1}$  と有機電解液に匹敵する特性を有し、しかも、環境に対する安定性が高く、リチウム電池の電解質として期待されている。

## 【0012】

【発明が解決しようとする課題】しかしながら、前記酸化物系無機固体電解質は脆性材料であるために機械的性質に乏しく、薄形化が困難であるという課題があった。

【0013】この課題を解消すべく、酸化物系無機固体電解質に可撓性を付与することが考えられる。

【0014】すなわち、高分子化合物を混合するとリチウムイオン伝導性酸化物系無機固体電解質の粒子表面は絶縁性の高分子化合物に覆われた状態となり、酸化物系無機固体電解質に可撓性が付与されるが、その反面、酸化物系無機固体電解質の粒子間のイオン伝導が阻害され、リチウムイオン伝導性酸化物系無機固体電解質と高分子化合物の複合体のイオン伝導度が低くなっていた。

【0015】本発明は叙上に鑑み完成されたものであり、その目的は可撓性に優れ、高い充放電性能をもつリチウム電池を提供することにある。

## 【0016】

【課題を解決するための手段】本発明の請求項 1 に係るリチウム電池は、リチウムイオンの可逆的な吸蔵放出が可能な活物質からなる正極と負極との間に、リチウムイオン伝導性を有する酸化物系無機固体電解質からなる固体電解質を配設してなり、そして、上記活物質と酸化物系無機固体電解質との間に、環状で環内に C=C 不飽和結合を有するエステルもしくはその誘導体の重合体が介

にしていることを特徴とする。

【0017】本発明の請求項2に係るリチウム電池は、上記の如き本発明のリチウム電池において、酸化物系無機固体電解質がリチウム(Li)、チタン(Ti)、リン(P)、および酸素(O)元素を含むリチウムイオン伝導性酸化物結晶であることを特徴とする。

【0018】また、本発明の請求項3に係るリチウム電池は、上記の如き本発明のリチウム電池において、前記正極および負極の活物質が  $Li_{1-x}Mn_{2-x}O_4$  ( $0 \leq x \leq 0.2$ )、 $LiMn_{2-y}Me_yO_4$  ( $Me=Ni, Cr, Cu, Zn, 0 \leq y \leq 0.6$ )、 $Li_xMn_5O_{12}$  および  $Li_xTi_5O_{12}$  よりなる群から選択される少なくとも1種類からなることを特徴とする。

【0019】

【発明の実施の形態】以下、本発明のリチウム電池の実施形態について説明する。図1は本発明に係るリチウム電池の構成例を示す断面図である。

【0020】1は正極集電体、2は正極、3は固体電解質、4は負極、5は負極集電体、6は電槽であり、正極2と負極4との間に、リチウムイオン伝導性を有する酸化物系無機固体電解質からなる固体電解質3を配設し、正極2の外面に正極集電体1を設け、負極4の外面に負極集電体5を設けた構造である。そして、この構造を電槽6でもって囲んでいる。

【0021】正極2および負極4に用いる活物質としては、次のような遷移金属酸化物が挙げられる。

【0022】例えば、リチウムマンガン複合酸化物、リチウムニッケル複合酸化物、リチウムコバルト複合酸化物、リチウムニッケルコバルト複合酸化物、リチウムバナジウム複合酸化物、リチウムチタン複合酸化物などとそれらの誘導体が挙げられる。

【0023】上記の遷移金属酸化物のうち、特に  $Li_{1-x}Mn_{2-x}O_4$  ( $0 \leq x \leq 0.2$ )、 $LiMn_{2-y}Me_yO_4$  ( $Me=Ni, Cr, Cu, Zn, 0 \leq y \leq 0.6$ )、 $Li_xMn_5O_{12}$  および  $Li_xTi_5O_{12}$  よりなる群は、充放電中の活物質の体積変化が小さい、結晶系がスピネル系の活物質であり、良好なサイクル特性を示す点でよい。

【0024】固体電解質3に用いられる酸化物系無機固体電解質には、例えば  $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$  や  $Li_{3.6}Ge_{0.6}V_{0.4}O_4$  などの結晶質固体電解質、 $30LiI-41Li_2O-29P_2O_5$  や  $40Li_2O-35B_2O_3-25LiNbO_3$ 、 $10Li_2O-25B_2O_3-15SiO_2-50ZnO$  などの非晶質固体電解質、あるいは結晶質固体電解質と非晶質固体電解質の混合体もしくは焼成体を挙げることができる。

【0025】しかし、非晶質で酸化物系の固体電解質は、リチウムイオン伝導度が室温で  $1 \times 10^{-6} S \cdot cm^{-1}$  程度であり、十分に特性を満たす固体電解質は見出されていない。これに対して、結晶質の固体電解質は室温

でのリチウムイオン伝導度が  $1 \times 10^{-4} \sim 10^{-3} S \cdot cm^{-1}$  と有機電解液に匹敵する特性を有している。

【0026】結晶質で酸化物系の固体電解質の中でも、特にリチウム(Li)、チタン(Ti)、リン(P)および酸素(O)元素を含むリチウムイオン伝導性の結晶質の固体電解質は化学的安定性、イオン伝導性の双方とも優れる点で好ましい。

【0027】具体的には  $Li_{1-x}M_xTi_{2-x}(PO_4)_3$  ( $M=Al, Sc, Y, La$ )、 $Li_{1-x}Ti_{2-x}(PO_4)_3$ 、 $Li_{0.5-3x}R_{0.5+x}TiO_3$  ( $R=La, Pr, Nd, Sm$ )、 $Li_{1-x-y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$ 、 $Li_{1-(4-n)}M_xTi_{2-x}(PO_4)_3$  ( $M$ は1価または2価の陽イオン)などが挙げられる。

【0028】これら正極活物質、負極活物質、および酸化物系無機固体電解質の粒子を結着する結着材としては、環状で環内にC=C不飽和結合を有するエステルまたはその誘導体の重合体が用いられる。

【0029】このような重合体はリチウムイオン伝導に寄与し得る酸素原子を高密度に有し、かつ可撓性のある材料である。その重合体が活物質および酸化物系無機固体電解質粒子の接触点近傍に存在することで、粒子間のリチウムイオン伝導に対する抵抗が低減され、高性能で、加工性に優れた電池が得られる。

【0030】前記重合体の前駆体である、環状で環内にC=C不飽和結合を有するエステルとしては、例えば、ビニレンカーボネート、クマリン、カテコールカーボネート、フタリドなどが挙げられ、その誘導体としては、例えばアルキル置換基ビニレンカーボネート、アルキル置換基カテコールカーボネートなどが挙げられる。

【0031】上記環状のエステルまたはその誘導体の環内のC=C不飽和結合は重合体が形成されやすいよう共鳴構造でないことが望ましく、また、リチウムイオン伝導性に優れるカーボネート構造であることが好ましい。従って、環状で環内にC=C不飽和結合を有するエステルまたはその誘導体としては、特にビニレンカーボネートまたはその誘導体が望ましい。

【0032】上記重合体の重合反応に使用される重合開始剤としては、例えば、過硫酸カリウム、過硫酸ナトリウム、過硫酸水素、アゾビスイソブチロニトリル、ベンゾイルパーオキシドなどのラジカル重合剤が挙げられる。

【0033】また、上記重合体の可撓性を高めるべく、微量の可塑剤を添加してもよい。この場合の好適な可塑剤としては、エチレンカーボネート、プロピレンカーボネート、ブチレンカーボネート、γ-ブチロラクトン、テトラヒドロフラン、2-メチルテトラヒドロフラン、1,2-ジメトキシエタン、1,3-ジオキソラン、スルホラン、ビニレンカーボネートなどが挙げられる。これらの可塑剤は1種単独を添加してもよく、必要に応じて2種以上を併用添加してもよい。

【0034】正極および負極活物質、酸化物系無機固体電解質の粒子間への重合体の添加方法としては、例えば、正極活物質、酸化物系無機固体電解質、負極活物質の粉末を三層に加圧成型または焼成した後、これに前記重合体の前駆体を含浸、重合させる方法などが挙げられる。

【0035】また、正極および負極中には電子伝導剤として、導電性酸化物や炭素材料、金属粉を混ぜてもよい。導電性酸化物では、例えば、 $\text{SnO}_2$ 、 $\text{In}_2\text{O}_3$ 、 $\text{TiO}_2-x$ 、 $\text{ZnO}$ 、 $\text{Fe}_3\text{O}_4$ 、 $\text{ReO}_3$ 、 $\text{MoO}_2$ 、 $\text{RuO}_2$ 、 $\text{VO}$ 、 $\text{WO}_2$ などが挙げられる。

【0036】かかる炭素材料として、例えばファーンズブラックやアセチレンブラック、サーマルブラックなどのカーボンブラックと鱗片状や繊維状の天然黒鉛や人造黒鉛などを挙げるができる。

【0037】さらに金属粉では、例えば、 $\text{Au}$ や $\text{Ag}$ 、 $\text{Al}$ 、 $\text{Cu}$ 、 $\text{Ni}$ 、 $\text{Fe}$ などを挙げるができる。

【0038】また、正極活物質、負極活物質、酸化物系無機固体電解質の粒子の焼結の際には、酸化物ガラスを使用してもよい。酸化物ガラスとしては、例えばリン酸塩ガラスやホウ酸塩ガラス、ケイ酸塩ガラス、ホウケイ酸塩ガラスを中心とした多成分系酸化物ガラスを挙げるができる。

【0039】正極集電体1と負極集電体5に用いる金属薄板はステンレス、アルミニウム、ニッケル、銅、コバルト、42アロイ、チタンあるいはアルミニウム合金などの金属材料でもって構成すればよい。

【0040】電槽6としては、例えばアルミニウム箔とポリエチレンとを積層したラミネートフィルムなどが用いられる。

【0041】かくして本発明のリチウム電池によれば、正極活物質、負極活物質、および酸化物系無機固体電解質の粒子を結着する結着材としては、環状で環内にC=C不飽和結合を有するエステルまたはその誘導体の重合体が用いたことで、優れた可撓性が得られ、そして、高い充放電性能が達成できる。

【0042】

【実施例】正極、負極、および酸化物系無機固体電解質からなる積層体にビニレンカーボネートを含浸、重合させることにより、本発明のリチウム電池Aを作製した。

【0043】このリチウム電池Aの具体的構成は下記の通りである。正極および負極活物質である $\text{Li}_{1-x}\text{Mn}_{1-y}\text{O}_2$ と酸化物ガラスである $50\text{P}_2\text{O}_5-30\text{PbO}-20\text{ZnO}$ を重量比95:5で乾式混合して混合粉とした。この混合粉100に対して成形助剤のエチルセルロースが重量比で10となるように加え、さらにテレピネオールおよびトルエンを加えて混合し、スラリーを調製した。このスラリーをポリエチレンテレフタレート（PET）フィルム上に塗布して乾燥させた後に裁断したものを650℃にて加熱焼成することで正極および負極成

形体を得た。

【0044】酸化物系無機固体電解質である $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-y}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ （ $0 \leq x \leq 0.4$ 、 $0 \leq y \leq 0.6$ ）と酸化物ガラスである $50\text{P}_2\text{O}_5-30\text{PbO}-20\text{ZnO}$ を重量比90:10で乾式混合して混合粉とした。この混合粉100に対して成形助剤のエチルセルロースが重量比で10となるように加え、さらにテレピネオールおよびトルエンを加えて混合し、スラリーを調製した。このスラリーを正極および負極成形体上に塗布して貼り合わせた後、600℃にて加熱焼成することで三層積層体を得た。

【0045】積層体の厚みは正極および負極が75μm、酸化物系無機固体電解質が50μmであった。

【0046】アルゴン雰囲気中、ビニレンカーボネートにラジカル重合開始剤であるベンゾイルパーオキシドを0.5wt%添加した後、これを真空加熱により脱水処理を施した上記三層積層体中に含浸させた。さらにアルゴン雰囲気中60℃にて20時間加熱して、ビニレンカーボネートの重合処理を行い、発電素子を形成した。

【0047】上記発電素子を15×20mmに裁断した後、正極および負極にニッケル板の集電体を張り付け、アルミニウム-ポリエチレンラミネートフィルムを加熱融着することで電槽を形成した。電槽の寸法は25×30mmとした。

【0048】[比較例1]比較例1として、上記リチウム電池Aと同じ三層積層体を用い、実施例と同様にしてビニレンカーボネートの重合体を含有しないリチウム電池Bを作製した。

【0049】[比較例2]比較例2として、上記リチウム電池Aと同じ三層積層体を用い、三層積層体内部にスチレンを含浸し重合したこと以外は実施例と同様にしてポリスチレンを含有するリチウム電池Cを作製した。

【0050】これらのリチウム電池A、BおよびCについて、その可撓性を調べるために、曲げ試験を行った。曲げ試験は長辺方向のたわみを5mmとして3回行い、それぞれの電池の内部の三層積層体の状態を目視した。

【0051】その結果、比較例のリチウム電池Bでは積層体に割れが見られたのに対し、本実施例におけるリチウム電池AおよびCの積層体は、曲げ試験によっても外観上は異常が見られず、高い可撓性を有していることが明らかとなった。

【0052】また、これらのリチウム電池A、BおよびCについて充放電測定を行い、放電容量を求めた。

【0053】各リチウム電池の放電容量は充電終止電圧を2.0V、電流値を100μAとして定電流充電した後、1時間放置して電流値100μAにて0Vまで定電流放電して求めた。その結果を表1に示す。

【0054】

【表1】

電池名称	放電容量 (mAh)
リチウム電池 A	4.2
リチウム電池 B	動作しない
リチウム電池 C	動作しない

【0055】表1から分かるように、正極、負極、および酸化物系無機固体電解質からなる三層積層体中にビニレンカーボネートを含浸、重合させたリチウム電池Aでは、ビニレンカーボネートの重合体を含有していないリチウム電池Bおよびポリスチレンを含有しているリチウム電池Cに比べて充放電特性が大きく向上した。

【0056】本発明者は活物質および酸化物系無機固体電解質の粒子の接触点近傍に、リチウムイオン伝導に寄与し得る酸素原子を高密度に有するビニレンカーボネートの重合体が存在することで、粒子間のリチウムイオン伝導に対する抵抗が低減されたためであると考える。

【0057】なお、本発明は上記のような実施形態例に限定されるものではなく、本発明の要旨を逸脱しない範囲で種々の変更や改良を加えることは何ら差し支えない。

【0058】

【発明の効果】以上のように、本発明によれば、リチウ\*

\* ムイオンの可逆的な吸蔵放出が可能な活物質からなる正極と負極との間にリチウムイオン伝導性を有する酸化物系無機固体電解質を配設してなるリチウム電池において、前記活物質粒子および酸化物系無機固体電解質粒子の間に、環状で環内にC=C不飽和結合を有するエステルまたはその誘導体の重合体が介在していることによって、高性能で、かつ機械的性質、加工性に優れたリチウム電池が得られ、これによって高い充放電性能が達成できた。

【0059】

【図面の簡単な説明】

【図1】本発明のリチウム電池の構成例を示す断面図である。

【符号の説明】

1：正極集電体、2：正極、3：固体電解質、4：負極、5：負極集電体、6：電槽

【図1】

